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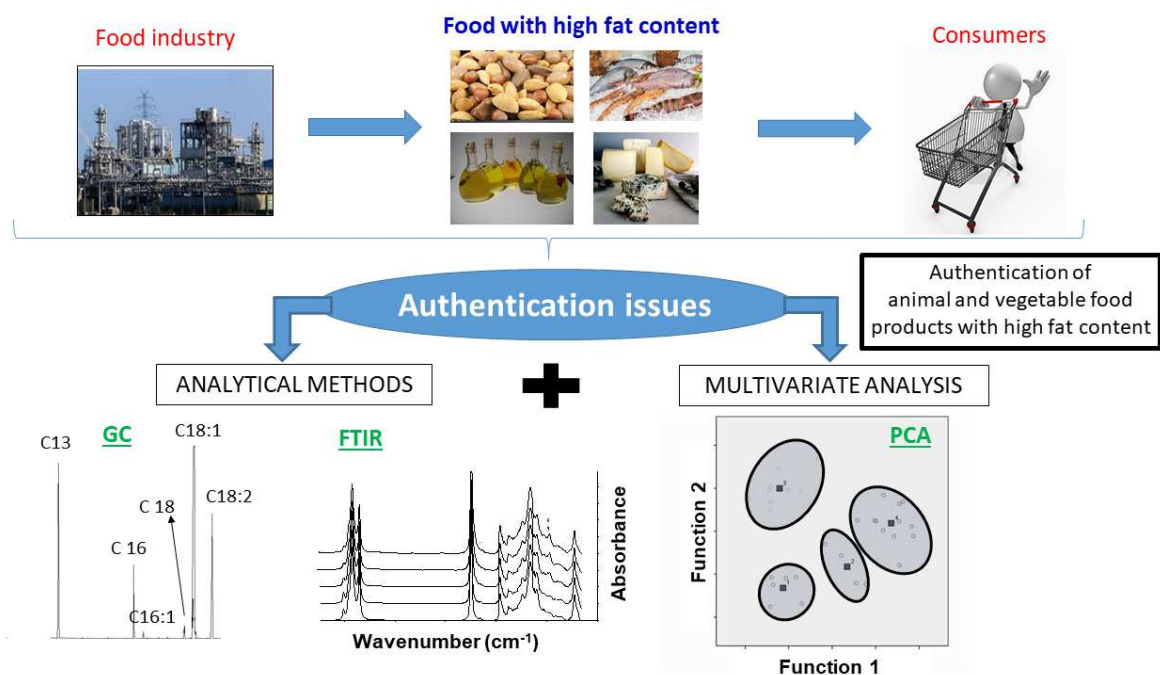
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**Analytical methods combined with multivariate analysis for
authentication of animal and vegetable food products with high fat
content**

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Abstract

Background: Food fraud is described as a violation of food law, which is intentionally committed to get an economic or financial gain through the consumer's swindle resulting in multi-million business and posing a public health threat. The main fraudulent practices are mislabelling of composition, certificates of origin, health claims, and artificial increases in weight or volume caused by replacement, dilution, addition or removal of some ingredients. Hardly 68% of the food fraud violations are produced in animal and vegetable products with high fat content (27% meat, 13% fish, 11% oils, 10% dairy products, 4% nuts and seeds and 3% animal by-products) becoming a crucial issue for food processing industries.

Scope and approach: The present review focuses on the main authentication techniques and methods employed to clarify the authenticity of both animal and vegetable fat food products emphasizing the importance of the use of robust and reliable analytical techniques combined with multivariate analyses.

Key findings and conclusions: Targeted approaches, such as chromatography and DNA-based methods, combined with multivariate analysis have shown high accuracy, sensitivity and selectivity, allowing the simultaneous evaluation of multiple analytes. In addition, non-target methods, such as those based on spectroscopic techniques, have been used to establish the geographic origin of food products with quick response, low cost, non-destructive character and also offering the possibility to be miniaturized.

Keywords: Food authentication, Animal products, Vegetable oils and nuts, Geographical Origin, Analytical techniques, Multivariate analysis.

1. Introduction

The authentication of food products is of the outermost importance for the food industry, not only for economical but also for health safety reasons (Abbas, Zadavec, Baeten, Mikuš, Lešić, et al., 2018). Food fraud is a long-term practice that has become a global public health and economical problem. Recent rises in these practices have been observed by the increase in the complexity in the food supply chain, getting from local to global dimension and linked with the motivation to provide cheaper and high quality food products (King, et al., 2017). The National Sanitation Foundation (NSF) has recently estimated that food fraud practices set up for the industry an annual cost of above 49 billion dollars worldwide (NSF, 2017). Although there is no a specific and harmonised definition for food fraud, it is broadly accepted that it is committed by an intentional violation of food law to obtain financial gain resulting in consumer's health risk and deception (Commission, 2017; van Ruth, Huisman, & Luning, 2017). Only in the European Union, 177 cases of fraudulent practices were reported in 2016 by the Administrative Assistance and Cooperation System available for EU Member States while five major alleged violations in food safety and quality were reported by Member States (Figure 1) (Commission, 2016).

Figure 1

Authentication of food products can be interpreted as verifying the product labels, tracing the origin of food and/or confirming the presence of those ingredients intended to be in their composition (Abbas, Zadavec, Baeten, Mikuš, Lešić, et al., 2018). The alleged food fraud violations can be highly varied, such as mislabelling of composition, denomination, health claims, quality terms, quantity weight or volume,

manipulation of documents, practise of unapproved treatments and/or processes, intellectual property infringement of trademarks, denomination of origin and/or geographical indications. Although most of food frauds are not potentially harmful for consumers, some of them could represent a public health risk (Weng & Neethirajan, 2017). Thus, food producers must ensure that all consumers are given comprehensive information on ingredients in the product label, making easier for citizens with food allergies or intolerances to identify ingredients to avoid (FALCPA, 2004). Figure 2 shows that hardly 68% of all food fraud cases in 2016 were reported in animal and vegetable food products with high fat content (27% meat, 13% fish, 11% fats and oils, 10% milk and milk products, 4% nuts, nut products and seeds and, finally, 3% animal by-products) (Commission, 2016).

Figure 2

A similar trend has been reported in other countries. The UK Food Standards Agency (FSA) reported in 2015 a warning recall of commercial palm oil by its content in the potentially genotoxic and carcinogenic red dye known as Sudan IV, (FSA, 2015). Some cases were also reported in the United States. For instance, 1,500 lbs of whole, young chicken were retired by their contamination by veterinary drugs (nitrofurazone) in 2017 (Landburg & Fodevarer, 2017). In India, milk, khoya and edible oils have been adulterated (Sarda, 2017). Zhang and Xue recently analysed 1553 media reports of food frauds in China reporting that animal food products including meat, fish, seafood and dairy products (38%), cooking oils (5%) and nuts and seeds (2%) are highly susceptible to adulterations (Zhang & Xue, 2016). Hence, authorities are required to be able to assess the authenticity of a suspect food products regarding the legal product description to

detect fraudulent processing features, preventing adulteration and controlling those practices which may mislead the consumer, such as mislabelling of geographical origin or composition of the product (Abbas, et al., 2018; Weng & Neethirajan, 2017).

The aim of this study is to provide an overview of the currently available tools for the authentication of animal and vegetable food products with high fat content (meat, fish, dairy products, vegetable oils and nuts), emphasizing the use of analytical techniques combined with multivariate analysis. These strategies result in improving the control in the food processing technologies by providing more informative results and increasing the reliability of foodstuff specifications as compared to using a single analytical technique. In this review, the most significant analytical methods using chromatography, spectroscopy and DNA techniques, among others, have been reported as successful in food authentication. However, the reported work is mainly focused on research with no much information about the implementation of these strategies by food industry for routine analysis since the validation, costs and availability of instrumentation must be considered.

2. Authentication of animal fat food products.

2.1. Meat food products.

Consumers require clear and reliable information about meat products that must be detailed in labelling in accordance with the applicable laws and regulations. This requirement has a great impact on food industry since the consumer's choice is greatly influenced by the food composition (Iammarino, Marino, & Albenzio, 2017). However, some fraudulent practices in the meat industry have been identified: a) Origin authentication of meat and the animal feeding regime (as in the case of certified regional products); b) substitution of meat ingredients by other animal species, i.e. tissues, fat or

proteins; c) modification of the processing methods; and d) addition of non-meat components, such as water or additives (Sentandreu & Sentandreu, 2014). Table 1 summarizes the main authentication methods and techniques currently used in meat products.

Table 1

European quality systems have identified specific meat-based products, such as those linked to their Protected Denomination Origin (PDO), Protected Geographical Indication (PGI) and Traditional Specialities Guaranteed (TSG). As an example, dry-cured ham is highly susceptible to fraud by its high nutritional value and numerous health benefits due to the presence of high amount of unsaturated fatty acids as well as folic acid in its composition (Bayés-García, et al., 2016). A recent study on the authentication of 24 Iberian ham samples by using headspace gas chromatography-ion mobility spectrometry (HS-GC-IMS) and principal component analysis (PCA) has been recently reported (Arroyo-Manzanares, et al., 2018). Individual PCA for each ham category with confidence intervals higher than 95% was carried out to detect possible outliers. The total information obtained for each sample was not used for data treatment; just the selection of significant markers was used, which are dependent on the type of column used in the chromatography study: in polar columns octanal or nonanal were used while in non-polar columns the main markers were octan-2-one and trans-2-octenal. 100% of all ham samples were correctly classified, including individual signals from their topographic plot samples. In general terms, the combination of chromatographic methods with mass spectrometry detection allows the simultaneous

determination of multiple analytes showing great potential for authentication in meat products, such as bolognese sauce (Prandi, et al., 2017).

DNA-based methods, mainly polymerase chain reaction (PCR), are increasing their use for the determination of the origin and quality of meat products (Kaltenbrunner, Hochegger, & Cichna-Markl, 2018; Prusakova, et al., 2018; Yalçinkaya, Yumbul, Mozioglu, & Akgoz, 2017). However, these methods are time-consuming, laborious and require costly chemicals (Kumar & Chandrakant Karne, 2017). Thus, alternative analytical techniques in combination with chemometric methods have been developed. In this sense, the potential of laser induced breakdown spectroscopy (LIBS) combined with PCA and partial least squares (PLS) methods has been evaluated as a rapid *in-situ* method to identify meat species in the 350-889 nm spectral region (Bilge, Velioglu, Sezer, Eseller, & Boyaci, 2016). Copper has been used for detecting adulteration of beef meat by the addition of beef liver, using the copper content as an indicator of the quality of meat (Casado-Gavalda, et al., 2017).

The evaluation of adulteration in meat products can be also based on the use of biosensors for detection of toxins and foodborne pathogens (Inbaraj & Chen, 2016). The haemoglobin present in blood was selectively adsorbed by graphene oxide particles functionalized with amylopectin and was detected by direct internal extractive electrospray ionization mass spectrometry (iEESI-MS) (Song, et al., 2017). Gold nanoparticles have been also used to develop a rapid immunosensor test to detect low levels of pork adulteration in beef meatballs using anti-Swine IgG polyclonal antibodies (Kuswandi, Gani, & Ahmad, 2017). All these examples are indicative of the potential use of nanotechnology to improve detection of frauds in meat products when used in combination with chemometric tools.

The addition of salts to increase the water holding capacity of meat is also a fraudulent practice related to artificial weight gain with commercial purposes. In this context, the detection and determination of adulterated bovine meat samples by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) can be considered as a complementary technique to the official testing method. Five parameters (protein, chloride, phosphate, sodium and ash contents) are determined (Nunes, Andrade, Santos Filho, Lasmar, & Sena, 2016). In fact, partial least squares-discriminant analysis (PLS-DA) was used to classify samples by merging physico-chemical parameters and FTIR spectra. The FTIR vibrations of aggregated β -sheets of proteins (specific band at 1690 cm^{-1}) were associated to the effect of the addition of sodium chloride to meat, since it could produce changes in proteins conformation. These results were applied to the study of a real case in Brazil resulting in a low cost, rapid, simple, and non-destructive technique.

It has been stated that the addition of salt to meat products produces changes in the secondary structure of the proteins, modifying the values obtained by FTIR regarding the amide I region, specifically due to the variation in the C=O stretching band (Perisic, Afseth, Ofstad & Kohler, 2011; Perisic, Afseth, Ofstad, Narum & Kohler, 2013). The amide I region, it is by far the best characterized band with respect to conformational studies of proteins and it is commonly used in secondary structure analyses. As a result of the high protein content in meats, absorption in this region can be expected in all types of meat and instruments. Nevertheless, it should be checked if the changes produced in the proteins conformational structure are enough to detect the addition of other components by themselves or further data in other regions should be obtained, for example, the amide region II (Li-Chan, Chalmers & Griffiths, 2011).

Regarding substitutions of meat ingredients by other animal species, such as tissues, fat or proteins, some authors have reported recent studies in pork (Al-Kahtani, Ismail, & Asif Ahmed, 2017; Yacoub & Sadek, 2017). In this context, a recent review explaining all DNA-based techniques used for the study of meat authenticity has been recently published (El Sheikha, et al., 2017).

2.2. Fish food products

Fish consumption has risen due to its high nutritional value, strong aquaculture supply and firm demand; record hauls for some key species and reduced wastage as indicated by the Food and Agriculture Organization of the United Nations (FAO, 2016). However, fish and seafood products are highly perishable due to their high-water activity, low content of connective tissue, neutral pH and the presence of autolytic enzymes in their composition. Conversely, adequate treatments, such as freezing and thawing, are required to maintain their quality and reduce spoilage (Hassoun & Karoui, 2017; Karoui, Hassoun, & Ethuin, 2017). Differences between fresh and frozen-thawed fish are required for their commercial distribution and spectroscopic techniques provide high specificity and quick response for such purpose (Karoui, et al., 2017; Reis, et al., 2017; Velioğlu, Temiz, & Boyaci, 2015). Reis *et al* (Reis, et al., 2017) applied visible-near infrared radiation (Vis-NIRS) and PLS-DA to classify samples based on frozen tuna. Spectral bands at 495, 550 and 590 nm were associated with changes in the myoglobin content. Bands in the region around 765 nm (associated with the water content) and 1360 nm (1st overtones from -CH in -CH, -CH₂ and -CH₃ groups) were also detected and attributed to specific structures in frozen fish. These modifications in the fish tissues structure is related with freezing by the formation of ice and increase in

the water volume resulting in changes on structure and composition of frozen fish samples.

Table 2 summarizes the latest reports regarding the use of different techniques and predictors for the authentication studies and detection of frauds in fish products. Traditional identification by visual inspection becomes quite challenging for processed fish since the head, fins, skin or bones are modified for commercial distribution (Reinders, Banovi, Guerrero, & Krystallis, 2016).

Standard methods based on isotopic analysis by nuclear magnetic resonance (NMR) spectroscopy are routinely used in Europe and North America to evaluate the authenticity of processed fish products. Kim *et al* (Kim, Suresh Kumar, & Shin, 2015) studied the authenticity and traceability of seafood and aquaculture products using site-specific natural isotope fractionation (SNIF) coupled with NMR. Three varieties of marketable-sized commercial fish (Mackerel, Yellow Croaker and Pollock) obtained from four species (*Scomber japonicas*, *Larimichthys polyactis*, *Larimichthys crocea* and *Theragra chalcogramma*) were chosen for this study. The obtained ^{13}C -NMR and ^{15}N -NMR spectra exhibited significant differences based on their origin. The classification by ^{13}C -NMR of Mackerel varieties was related to the positive correlation between seawater temperature and intensity of some bands in the ^{13}C -NMR spectra. In this sense, some components in fish and seafood show their own range of naturally-occurring isotopic forms of carbon (^{12}C , ^{13}C), hydrogen (^1H , ^2H), oxygen (^{16}O , ^{18}O) and nitrogen (^{14}N , ^{15}N), which are influenced by physical, chemical and biochemical factors related to fish origin.

Table 2

Chang *et al.*, (Chang, Lin, Ren, Lin, & Shao, 2016) published a report regarding frauds in the labelling of seafood products in Taiwan. Results confirmed labelling modification on up to 70% of the analysed products based on a cytochrome c oxidase subunit 1 segment (COI) obtained by PCR. As indicated in Table 2, advances in PCR-based techniques stand out for their selectivity and effectiveness in detecting frauds in seafood labelling (Mazzeo & Siciliano, 2016).

Finally, handling of fish can become a significant problem since some seafood distributors inject substances (hydrocolloids or saline solutions) into the head and belly of crustaceans to improve weight and market prize with similar colour appearance and fresh look than unadulterated crustaceans (Li, Li, & Zhang, 2018). A recent study reporting adulteration in small yellow croakers by injecting an edible-gluten solution has been published (Zang, et al., 2017). Authors reported that low field ^1H NMR spectroscopy allows the determination of adulterated samples with a carrageen solution.

2.3. Dairy food products

Dairy products have high nutritional value as well as global production and consumption, either as raw milk or lacteous derivatives, make them highly susceptible to frauds (King, et al., 2017). The worldwide production of milk has increased from 624,282 to 657,671 million tonnes between 2013 and 2015 being the European Union the main producer followed by India, United States, China and Pakistan (OECD/FAO, 2016). A continuous growth of the dairy market is expected up to 2025, with annual increases of 2.0% for skim milk powder, 2.1% for whole milk powder, while butter and cheese production will increase at 1.7% and 1.4% yearly rate respectively.

Some issues on dairy products authentication were recently reported since the presence of substances different from those declared in label is a serious concern for

producers and consumers. Analytical methods for testing authenticity in dairy products include the analysis of ingredients and determination of geographical origin, as detailed in Table 3. (Nascimento, Santos, Pereira-Filho, & Rocha, 2017).

Table 3

The most hazardous fraud practice in dairy products is based on the increase of the protein fraction by addition of harmful nitrogenous melamine compounds. Indeed, the European Commission and the United States Food and Drug Administration (FDA) have considered a maximum acceptable limit of 2.5 mg kg^{-1} of melamine compounds in imported foods and 1 mg kg^{-1} in infant milk (Azad & Ahmed, 2016). LIBS and neural networks (NN) methods have been proposed as authentication tools for different semi-skimmed milks obtained from cow, goat and sheep. The direct measurement of their plasma emission in on-line systems has been proposed, obtaining 100% of discrimination between milk types with absorption bands from 190 to 450 nm (Moncayo, Manzoor, Rosales, Anzano, & Caceres, 2017). This experimental combination was also used to develop a calibration model to quantify the calcium content in infant milks (Cama-Moncunill, et al., 2017).

Other chemicals used in milk frauds (formaldehyde, sodium citrate, starch, hydrogen peroxide and sodium carbonate) were properly detected by measuring absorbance values of bands obtained in the mid-infrared (MIR) ($4000\text{-}400 \text{ cm}^{-1}$) region combined with a soft independent modelling by class analogy (SIMCA) prediction model. The cross-validation method for the construction of these models has been recently proposed as an adequate tool for elucidating structures of specific compounds in milk (Gondim, Junqueira, Souza, Ruisánchez, & Callao, 2017). MIR provides a large amount of chemical information regarding the studied sample by measuring relevant

fundamental vibrations instead of overtones and combination bands (Abbas, Zadavec, Baeten, Mikuš, Lešić, et al., 2018). Bands at 1086, 525 and 424 cm^{-1} allowed the detection of maltodextrin in low-lactose and whole milk powder samples. The adulteration of spreadable cheeses with starch was also detected by using bands at 2880, 1750, 1650, 1440 and 477 cm^{-1} as predictors (de Sá Oliveira, de Souza Callegaro, Stephani, Almeida, & de Oliveira, 2016). Raman spectroscopy has been widely used in combination with PCA and linear discriminant analysis (LDA) to determine the origin of dairy products by the determination of specific ingredients (Table 3).

Time domain nuclear magnetic resonance (^1H TD-NMR) combined with SIMCA and NN models were also reported as useful rapid sequential strategy for milk authentication with high predictability, sensitivity and specificity (Santos, Pereira-Filho, & Colnago, 2016). In this study, five compounds undeclared in bovine milk label (urea, synthetic urine, whey, synthetic milk and hydrogen peroxide), were detected by using ^1H TD-NMR relaxation decay as discriminant parameters to provide information on diffusion, exchange processes and compartment sizes, being an extremely useful technique for measuring water and fat proportions in food. Li *et al.* (Li, et al., 2017) developed 1D and 2D-NMR methods combined with PCA to determine the origin of bovine and goat high-value milks while avoiding mislabelling due to the presence of undeclared soymilk. The first principal component (PC) accounted 83% of the total variance with high loadings of N-acetyl-carbohydrates, acetate, choline, ethanolamine, carnitine, citrate, creatine and lecithin, whereas the second PC accounted 11% of the total variance depending on D-sucrose and D-lactose.

Gas chromatography–flame ionization detection (GC-FID) and PLS-DA were proposed to detect milk frauds by adding whey by using fatty acids profile (myristic, linoleic, palmitic, elaidic, oleic and linolenic) obtaining significant differences in

composition between samples (de Oliveira Mendes, Porto, Bell, Perrone, & de Oliveira, 2016). In addition, differences in peaks intensities of fatty acids determined by capillary zone electrophoresis (CZE) combined with multiple linear regression (MLR) equations allowed to obtain high correlation coefficients, resulting in an advantageous methodology to detect different whey fractions in milk.

Authentication of milk of animal origin by the determination of specific fatty acids has been widely studied. The determination of specific ingredients from vegetable oils (coconut, soybean, palm, sunflower, peanut or groundnut) and animal fats from cow tallow or pork lard in different milk compositions has been recently reported (Trbović, Petronijević, & Dordević, 2017). GC can be applied in combination with PCA to determine milk composition and label statements with classification models based on fatty acids concentration as predictors (Table 3).

Inductively coupled plasma-mass spectrometry (ICP-MS) is a robust analytical technique to obtain useful information of samples composition without using complicated pre-treatments and providing accurate data based on mineral and trace elements. Table 3 also summarizes the main applications of ICP-MS in combination with multivariate analysis for origin authentication purposes in dairy products (Magdas, et al., 2016; Nečemer, Potočnik, & Ogrinc, 2016; Rodríguez-Bermúdez, et al., 2018; Zain, Behkami, Bakirdere, & Koki, 2016).

Finally, authentication issues have increased due to the addition of low-cost butterfat to high valuable cheese products. The addition of vegetable fats affects the thermal profile of cheese. Differential scanning calorimetry (DSC) coupled with cluster analysis can be used as a method to ensure the composition of fresh cheeses avoiding frauds by the addition of vegetable fats. Melting temperatures and enthalpy values were considered for such purpose obtaining 100% discrimination between genuine and

adulterated cheeses (Herman-Lara, et al., 2017). This strategy could be proposed as an alternative analytical method for cheese authentication with several advantages such as the minimal pre-treatment of samples, reduction of the analysis time and no need of solvents, reagents and standards for tests.

3. Authentication of vegetable fat food products.

3.1. Vegetable oils

Worldwide production of vegetable oils has undergone a significant growth from 148.77 to 185.78 million tonnes from 2010 to 2016 (Statista, 2017). Olive, coconut, sunflower seed, cottonseed, palm and palm kernel, soybean, peanut and rapeseed oils are produced all over the world rising 6.28% in the 2015-2016 time span. The increase in the vegetable oils production is linked to consumption as healthy alternative to animal fats by their higher amount in unsaturated fatty acids in their composition. Table 4 summarizes some examples of authentication methods and techniques used to detect frauds in vegetable oils.

Table 4

Chromatographic techniques in combination with chemometric analyses (mainly PCA followed by LDA or PLS) have been widely used to detect the fatty acid composition in different vegetable oils to identify their origin (Indelicato, et al., 2017; L. Zhang, et al., 2017). These techniques have been used in target approaches for the identification and quantification of specific analytes due to their high accuracy, selectivity and sensitivity. The use of NMR for identification of vegetable oils adulterations has been continuously rising by its environmentally-friendly character

showing unique and abundant information with low organic solvent consumption (Q. Li, et al., 2017). Gouilleux *et al.* (Gouilleux, Marchand, Charrier, Remaud, & Giraudeau, 2018) successfully applied an ultrafast 2D-NMR approach combined with PCA and PLS to classify vegetable oils from different botanical origins (hazelnut, corn, sunflower, sesame and rapeseed). Other authors used NMR combined with chemometric models in studies on the authentication of vegetable oils (Table 4) (Duarte, et al., 2016; Shi, et al., 2018; Zhu, Wang, & Chen, 2017).

Spectroscopy techniques have been widespread applied to obtain useful predictors to detect fraudulent practices in vegetable oils (Basri, et al., 2017; Ozulku, Yildirim, Toker, Karasu, & Durak, 2017) by their non-destructive nature, no need of sample preparation and toxic reagents, low cost and reproducibility. In this context, fluorescence and UV-VIS spectroscopy have been successfully used for the development of multivariate calibration models based on PLS and MLR methods to quantify potential adulterations in extra virgin olive oil (Milanez, et al., 2017). The fluorescence data attributed to phenolic compounds and tocopherols (300-390 nm), oxidation products of fatty acids (445-475 nm), vitamin E (525 nm), and degradation products of chlorophyll a and b (681 nm) were used as predictors. UV-VIS data (absorbance at 410, 450 and 470 nm for carotenoids and 660 nm for chlorophyll-rich compounds) were also used for the same purpose. Spectral data obtained from UV-VIS spectroscopy in combination with multivariate curve resolution methods (CR), PCA and LDA, were used for the evaluation of quality in virgin olive oils (Ferreiro-González, et al., 2017).

ICP-MS was used to determine the origin authenticity of Austrian pumpkin seed oil vs those produced in China and Russia (Zettl, Bandoniene, Meisel, Wegscheider, & Rantitsch, 2017). Authors proposed a method based on trace element data combined

with PCA followed by PLS working with up to 21 variables (Rb, Sr, Sm/Gd, Sr/Ba, Sr/Y, Sr/La, Sr/Ce, Sr/Pr, Sr/Nd, Sr/Eu, Sr/Sm, Sr/Gd, Sr/Tb, Sr/Dy, Sr/Ho, Sr/Er, Sr/Tm, Sr/Yb, Sr/Lu, Y/Ba and Y/U). The varietal origin of 49 different Turkish olive oils was successfully determined with their trace element contents (V, Mn, Ni, Cu, Ba, Na, K, Ca, Fe, Mg, Pb, As, Co, Cr, and Zn) by ICP-MS combined with PCA and hierarchical cluster analysis (HCA) chemometric tools (Gumus, Celenk, Tekin, Yurdakul, & Ertas, 2017).

Finally, DSC was used to detect differences between 39 extra virgin olive oil samples from different geographical areas (Tunisia, USA, Albania, Italy, Turkey, Greece and Spain). (Mallamace, et al., 2017). Authors focused on the oils melting parameters (temperatures and enthalpies of characteristic DSC peaks) by using 7 PCs obtained from PCA. They could justify 98% of the total variance with very low sample amounts (5-10 mg) and short experimental times (20-30 min). Thermal stability obtained by DSC coupled with fluorescence, absorbance, phenolics contents and antioxidant activities were used as predictors in PCA and cluster analyses to obtain differences between genotypes from 18 different orchards of Mexican avocado oils with the fluorescence emission as the most predictive attribute (Espinosa-Alonso, Paredes-López, Valdez-Morales, & Oomah, 2017).

3.2. Nuts and products

According to the more recent data by the International Nut and Dried Fruit (INC, 2017), the worldwide production of nuts has risen from 2.8 to approximately 4.2 million tonnes throughout the last decade. In the 2016/17 season, USA has been the major tree nut producer with a 41% share of the worldwide production. However, nuts should be considered as highly exposed to fraud practices since they can be relabelled with old or

expired stock samples or replaced with cheaper ones, representing serious problems to consumers by allergies and intolerances (Esteki, Van der Heyden, Farajmand, & Kolahderazi, 2017) (Table 5).

Table 5

Almonds constitute one of the most important nut products with a worldwide production amounted to approximately 1.09 million tonnes in the 2015/16 season (INC, 2017). The different growing conditions and climate, chemical composition, sensory, nutritional and health attributes are characteristic of each particular cultivar. The development of fast and low-cost detection methods for the origin determination of different almond cultivars has been a trending topic in the nut industry during the last decade (Valdés, Beltrán, & Garrigós, 2013). For instance, 23 almonds with different phenotypic groups from North Serbia were chosen and classified based on their fatty acid profile and their content in specific phenolic compounds (Čolić, et al., 2017). The total phenolic content, radical scavenging activity, oil content, 16 fatty acids and 28 polyphenols were included in the PCA. A 9-component model obtained by PCA explained 83% of the total variance, but results on the specific fatty acids and phenolics allowed the differentiation in 3 main genotype groups. Results for the total oil content and fatty acid profiles were combined with PCA to get differences between 15 almond cultivars based on 8 predictors: content of stearic, oleic, palmitic, palmitoleic and arachidic acid, total amount of unsaturated and saturated fatty acids and, finally, the unsaturated : saturated ratio (Yildirim, Akinci-Yildirim, Şan, & Sesli, 2016).

The combination of multi-elemental analyses based on inductively coupled plasma optical emission (ICP-OES) with PCA-LDA was applied to evaluate the almond powder

authentication. Almond powder is a high-price additive used in bakery and confectionery products, which is a target of illegal practices, such as mixing with cheaper nuts. PLS combined with least squares support vector machine (LS-SVM) was used to detect the presence of peanuts to avoid misleading labelling in almond powder. Contents of Sr, Ca, Fe, B, Na, Cu, Zn, Sr, Mg and K were used on the PCA allowing the classification of 100% of samples by LDA. This method has been also used to screen origin authenticity of other food products obtaining fingerprints of the element pattern for liquid and solid samples (Borràs, Ferré, Boqué, Mestres, Aceña, et al., 2015).

In a different study, PLS combined with LS-SVM was applied as a non-linear regression method giving information related with the level of peanut adulteration in almond mixtures (Esteki, Farajmand, Kolahderazi, & Simal-Gandara, 2017). Authors proposed a multivariate data analysis method based on the content of oleic, linoleic and palmitoleic acids for almond authentication avoiding frauds by the addition of apricot kernel.

The pistachio global production reached 760,000 tonnes in 2016 with a production focused on the USA followed by Iran and Turkey, that all together accounted for 94% of the world production (INC, 2017). Sensory analysis of nuts has gained importance as a valuable tool that allows the cultivar differentiation (Olsen, 2015). In fact, the sensory stability of 4 major commercial pistachio Iranian varieties (Kale-Ghouchi, Akbari, Ohadi and Momtaz) during storage was evaluated by using descriptive analysis combined with PCA, LDA and probabilistic neural network (PNN) (Ghasemi-Varnamkhasti, 2015). Some sensory attributes (bitterness, firmness, sweetness, rancidity, crunchiness, salty, sour, glossy and roasted taste) were evaluated by a professional trained panel to detect changes during 8-months storage.

The nut industry claims for the development of fast, easy and low-cost analytical methods to determine the authenticity of their products. FT-Raman hyperspectral imaging in combination with PCA and PLS has been recently reported as a useful technique to identify the presence of green pea granules in pistachio nut mixtures. The whole spectral NIR range (from 1100 to 2300 nm) was used in combination with PCA, allowing the classification of PDO 'Nocciola Romana' hazelnuts and separation from other cultivars (Moscetti, Radicetti, Monarca, Cecchini, & Massantini, 2015). This strategy is highly interesting since hazelnut is one of the most important raw materials for confectionary and bakery industries with a worldwide production of 397,160 tonnes in 2016, with the main production located in Turkey (INC, 2017). In other study, NIR spectra in the 896-1686 nm range of commercial cereals (barley, wheat, oat, rye, rice and corn), legumes and oilseeds (flax seed, soy, white chickpea, poppy, sesame, chia, rapeseed, cassava and sunflower) and, finally, nuts (almond and pine nut) were used to detect the presence of peanuts in other food products (Ghosh, et al., 2016). PCs obtained from 882 NIR spectra provided a primary classification of samples into categories, such as gluten, non-gluten, high fatty acid, high fibre and omega-3 fatty acid groups. In addition, 8 wavelength regions (960, 991, 1123, 1259, 1334, 1370, 1392, 1429 nm) allowed the segregation of almonds, peanuts, pine nuts, sesame and flaxseed by PLS-DA related with the protein and fat fractions in their composition. This study clearly demonstrated the power of the multivariate analyses to organise large amounts of data and to extract useful conclusions in the development of innovative strategies in the evaluation of fraudulent practices in the food industry. Finally, the application of non-destructive analytical methods by the detection of volatile compounds with e-nose signals combined with PCA, LDA, SVM and PLS methods allowed the identification of

the presence of non-fresh peanuts in fresh packages (Xu, Ye, Wang, Wei, & Cheng, 2017) showing potential as a non-destructive method to detect peanut quality.

Conclusions

Frauds in animal and vegetable food products with high fat content (including meat, fish, seafood, dairy products, vegetable oils, nuts and seeds) have increased in the last years becoming a serious concern for the food industry and consumers. This review has focused on the presentation of the most innovative studies in this context, where target and non-target analytical techniques combined with multivariate analysis have shown their potential in the authentication of food products with high fat content. Chromatography and DNA-based techniques have been used in combination with multivariate analysis, allowing the successful and simultaneous determination of multiple analytes with high accuracy, selectivity and sensitivity, resulting in a very powerful tool for authentication studies in food. Spectroscopy techniques are also useful for such purpose being mainly used to evaluate the geographical origin of specific food. These techniques are characterized by being fast, low-cost and, in most cases, non-destructive, so they could be easily implemented by industries in the next future. Research efforts in this area should go on since there are still some points to refine, such as the validation and scaling-up of all these methodologies. In addition, more efforts are necessary to address the development of portable instruments to implement these sophisticated authenticity tools in the routine analysis in the food industry.

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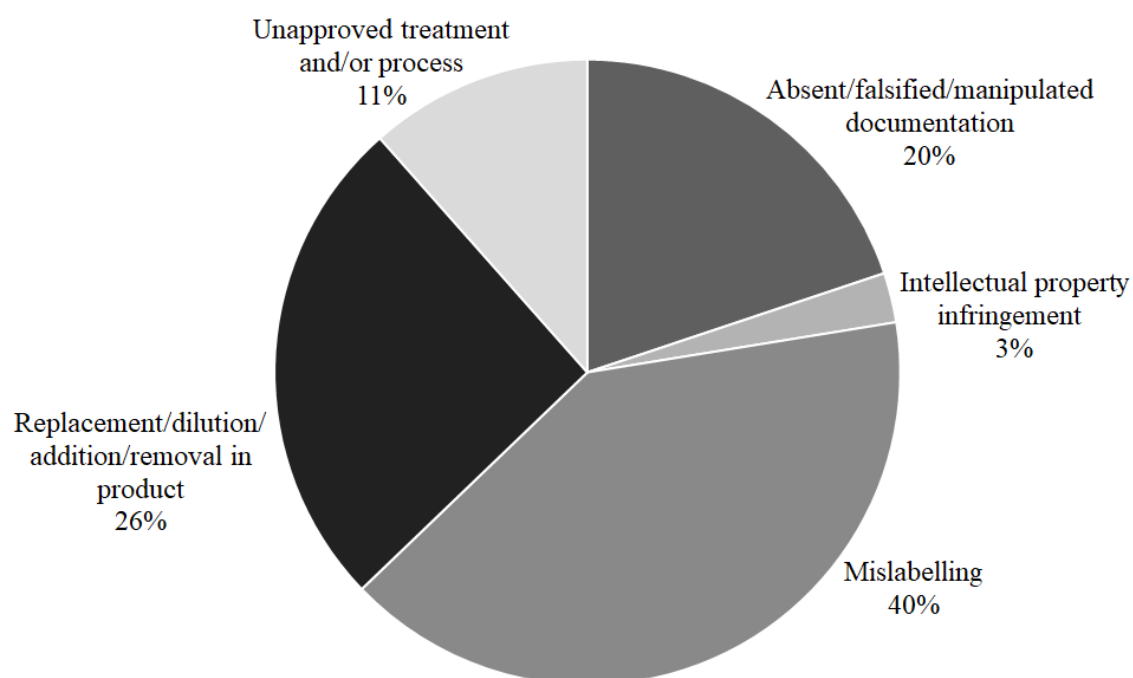
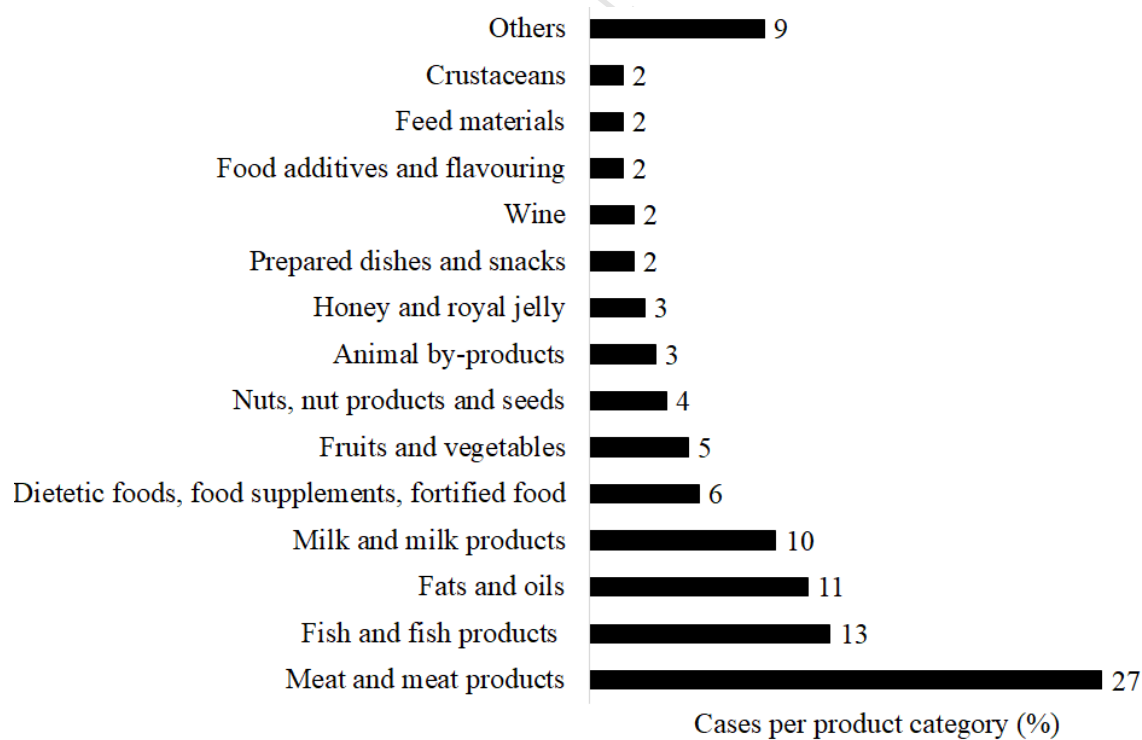
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Figure captions

Figure 1. Major alleged violations in food fraud by EU-Member States in 2016.

Figure 2. Cases of food fraud (%) per product category reported by EU-Member States in 2016.

859 **Figures**860
861 **Figure 1**863
864 **Figure 2**

865

Tables**Table 1**

Main methods and techniques used to detect frauds in meat products.

Meat product	Food fraud	Analytical technique	Predictors	Reference
Raw meat of chicken, turkey, goose, duck, quail and pigeon	Mammalian and poultry species	real-time PCR	Universal myostatin sequence	(Ren, et al., 2017)
Salami, sausages, cutlets, canned meat and frozen ready-to-cook food	Cat, dog, mouse, rat and human	Two-tube multiplex PCR	ATPase subunit 8 gene	(Prusakova, et al., 2018)
Raw meat of beef, pork and chicken	Vegetable protein, Wheat gluten	Vis-NIR with PCA	370-920 nm	(Rady & Adedeji, 2018)
Salami	Fraud in PDO, PGI and TSG	Chemical analysis with PCA	Sodium chloride, fat, protein, collagen and percent of protein without collagen contents	(Fekete, et al., 2016)
Sausages, frankfurters and pâtés;	Variation of the composition in the labelling	Protein quantification by nano-LC-QTOF-MS/MS	Specific-specific peptide marker	(Montowska & Fornal, 2017)
Fresh lean beef	Beef kidney	LIBS with PLS	Percentages of Na and K.	(Dixit, et al., 2017)
Bolognese sauce	Variation of the composition in the labelling	Protein quantification by UHPLC-ESI-MS	Peptide marker deriving from α 2-collagen chain.	(Prandi, et al., 2017)
Beef	Adulteration with pork and chicken	LIBS with PCA and PLS methods	350–889 nm spectral region	(Bilge, et al., 2016)
Fresh lean beef	Beef liver	LIBS with PLS	Cooper content	(Casado-Gavalda, et al., 2017)
Raw and boiled sheep meat	Authentication	Selective absorption and detection with iEESI-MS	Difference in molecular composition of haemoglobin	(Song, et al., 2017)

Abbreviations: Ultra-high-pressure liquid chromatography-MS-MS (UHPLC-MS-MS).

870 **Table 2**

871 Main methods and techniques used to detect frauds in fish products.

Fish product	Food fraud	Analytical technique	Predictors	Reference
Atlantic cod	Fraudulent substitution of this specie	Small Amplicons High Resolution Melting Analysis	Primers for the COI gene	(Tomás, Ferreira, & Faria, 2017)
Fresh and smoked specimens of Rainbow trout and Atlantic mackerel	Fraudulent substitution of this specie	DNA Extraction MALDI-TOF MS	cytb sequence	(Spielmann, et al., 2017)
Gadoid species	Authentication	High Resolution Melt and PCR Cytochrome Oxidase I Barcode-Restriction Fragment Length Polymorphism	Primers for the COI and cytb genes	(Fernandes, Costa, Oliveira, & Mafra, 2017)
White fish	Authentication		Primers for the COI gene	(Ferrito, Bertolino, & Pappalardo, 2016)
Fresh and frozen specimens of Salmon Horse mackerel Anchovy Red mullet Bluefish Flying gurnard	Differentiation of fresh and frozen-thawed fish samples Differentiation of different fish species	Raman spectroscopy with PCA	Spectra values from 200 to 2000 cm^{-1}	(Velioğlu, et al., 2015)
Sea bass (<i>Dicentrarchus labrax</i>)	Differentiation of fresh and frozen fish samples	Fluorescence spectroscopy and chemical analysis with PCA	Spectral bands at 290, 340, and 380 nm	(Karoui, et al., 2017)
Fresh fillets of <i>Gadus morhua</i> and <i>Melanogrammus aeglefinus</i>	Origin Authentication	NIR, PCA and SIMCA	Spectral bands at 970 nm and 1450 nm	(Grassi, Casiraghi, & Alamprese, 2018)
Different species of cod, fresh and patties	Authentication	Handheld NIR with PCA	Spectral bands at 950 nm and 1650 nm	(Grassi, et al., 2018)
Salmon	Origin Authentication	GC-MS/MS, PCA	Polychlorinated biphenyls (PCBs) and Polychlorinated dibenzo-p-dioxins	(Sørensen, Lund, Cederberg, & Ballin, 2016)

Small yellow croaker	Addition of carrageen solution	Low field ^1H NMR, PCR and PLS	and dibenzofurans (PCDD/Fs) Water and fat content and relaxation time about 2200 and 3330 ms	(Zang, et al., 2017)
Prawn	Injection of hydrocolloids	Low field ^1H NMR, PCA	Relaxation time between 10-200 ms and 700-1200 ms	(M. Li, et al., 2018)

Abbreviations: Gas chromatography–mass spectrometry detection (GC-MS).

892 **Table 3**
 893 Main methods and techniques used to detect frauds in dairy products.

Dairy product	Food fraud	Analytical technique	Predictors	Reference
Semi-skimmed milk from cow, goat and sheep	Melamine	LIBS combined with PCA and NN	Absorption bands from 190–450 nm	(Moncayo, et al., 2017)
Infant formula	Calcium	LIBS and PLS	Calcium emission at 423, 559, 612 and 617 nm, sodium line at 589 nm and potassium at 766 nm	(Cama-Moncunill, et al., 2017)
Cow milk	Starch, sodium carbonate, sucrose and sodium hydroxide	MIR and SIMCA	Absorbance values at 3400, 3000, 1700 and 1500 cm^{-1}	(Gondim, et al., 2017)
Spreadable cheese (whole and skimmed)	Starch	FTIR, PCA and PLS-DA	Bands at 2880, 1750, 1650, 1440 and 477 cm^{-1}	(de Sá Oliveira, et al., 2016)
Cow and buffalo milks	Soy milk	FTIR and PCA	Wave number range of 1680–1058 cm^{-1}	(Jaiswal, Jha, Borah, Gautam, Grewal, et al., 2015)
Pasteurized fat cream and skimmed cream	Addition of sunflower, coconut, palm oils	FTIR, PCA and LDA	Absorbance values of spectra bands of the fat fraction	(Nedeljkovic, Tomasevic, Miocinovic, & Pudja, 2017)
Milk of seven dairy animal groups (Chinese Holstein cow, Jersey cow, yak, buffalo, goat, camel, and horse)	Origin authentication	NMR combined with LC-MS and PCA, PLS-DA and OPLS-DA	Differential metabolites associated with metabolic pathways: (choline, succinic acid, glycerophospholipids, valine, leucine, isoleucine and unsaturated fatty acids)	(Yang, Zheng, Zhao, Zhang, Han, et al., 2016)
Bovine milk	Addition of water and adulterants	^1H TD-NMR, PCA, PLRS, SIMCA, and kNN	Relaxation time constants by PCA, full ^1H TD-NMR relaxation by PLRS, SIMCA and kNN	(Santos, et al., 2016)
Bovine and goat milk	Addition of soy milk	1D and 2D NMR and PCA	Acetyl-carbohydrates, acetate, choline, ethanolamine, carnitine, citrate, creatine and lecithin	(Q. Li, et al., 2017)
Milk	Whey addition	GC-FID and PLS-DA. CZE-UV and MLR	Fatty acids	(de Oliveira Mendes, et al., 2016)

Organic milk	Origin authentication	ICP-MS, PCA, HCA, DA, SIMCA and MLF-ANN	As, Co, Cr, Cu, I, Fe, Mn, Mo, Ni, Se and Zn content	(Rodríguez-Bermúdez, et al., 2018)
Cow Milk	Origin authentication	ICP-MS, PCA and HCA	Cl, Zn, P, Ca and K	(Nečemer, et al., 2016)
Sheep milk and cheese	Authentication	ICP-MS, PCA and HCA	P, S, K, Cl, Ca, Zn content and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in casein	(Nečemer, et al., 2016)
Milk	Origin authentication	ICP-MS, PCA and HCA	Ca, Na, Fe, Zn, Mn, K, Ba and Mg	(Zain, et al., 2016)
Bovine and Ovine milk	Origin authentication	ICP-MS and DA	Sr, Mn and isotopic ratios of oxygen and carbon markers	(Magdas, et al., 2016)
Cheese	Vegetable fat	GC-FID, DSC and cluster analysis	Fatty acids and melting temperature and enthalpy values	(Herman-Lara, et al., 2017)

Abbreviations: K- nearest neighbours (kNN); Multilayer feedforward artificial neural network (MLF-ANN).

Table 4

Main methods and techniques used to detect frauds in vegetable oils.

Vegetable oil	Food fraud	Analytical technique	Predictors	Reference
Vegetable edible oils	Authentication	Hyphenated techniques	Triacylglycerol's	(Indelicato, et al., 2017)
Virgin olive oil	Addition of soybean, rapeseed and maize oils	GC-MS and PLS	Fatty acids	(L. Zhang, et al., 2017)
Vegetable oils	Botanical authentication	2D NMR, PCA and PLS	2D-Peaks	(Gouilleux, et al., 2018)
Camellia oil	Addition of corn, sunflower and rapeseed oils	¹ H NMR, PCA, OPLS-DA and PLS	15 selected ¹ H NMR signals	(Shi, et al., 2018)
Peanut oil	Addition of soybean, rapeseed and palm oils	¹ H low-NMR, PCA and DA	LF-NMR parameters, single component relaxation time and peak area	(Zhu, et al., 2017)
Brazilian crude oil	Authentication	¹ H NMR and PLS	API gravity, carbon residue, wax appearance temperature and organic nitrogen	(Duarte, et al., 2016)
Palm oil	Lard	NIR spectroscopy, PCA and PLS	Spectra values from 900 to 1600 cm ⁻¹	(Basri, et al., 2017)
Sesame oil	Addition of hazelnut, canola, and sunflower oils	FTIR and PLS	Absorbance values at 1267-1209, 1121-1045, 876-814 cm ⁻¹	(Ozulku, et al., 2017)
Extra Virgin Olive Oil	Addition of soybean oil	Fluorescence and UV-Vis spectroscopy, PLS and MLR	Phenolics, tocopherols, fatty acids products, carotenoids, vitamin E and chlorophylls	(Milanez, et al., 2017)
Virgin Olive Oil	Origin authentication	Visible spectroscopy, CR, PCA y LDA	Chlorophylls and carotenoids spectra data	(Ferreiro-González, et al., 2017)
Pumpkin seed oils	Origin authentication	ICP-MS, PCA, PLS, SIMCA and SVM	Concentrations of 24 trace elements and 7 ratios of the element concentrations	(Zettl, et al., 2017)
Virgin olive oil	Geographical authentication	ICP-MS, PCA and HCA	Fe, Zn and $\delta^{13}\text{C}$	(Gumus, et al., 2017)
Organic olive oil	Origin authentication	DSC and PCA	Melting profiles of the triacylglycerols	(Mallamace, et al., 2017)
Avocado oil	Genotypes authentication	DSC, PCA and cluster	Fluorescence, absorbance, oxidative stability, phenolics, antioxidant activities, and thermal oxidation	(Espinosa-Alonso, et al., 2017)

914 **Table 5**

915 Main methods and techniques used to detect frauds in nuts.

Nut	Food fraud	Analytical technique	Predictors	Reference
Almond	Serbian genotypes authentication	UHPLC-MS/MS, GC-FID and PCA Soxhlet	Fatty acids and specific phenolic contents	(Čolić, et al., 2017)
	Cultivar authentication	extraction, GC-FID and PCA	Total oil content and fatty acid	(Yildirim, et al., 2016)
	Addition of peanut powder	ICP-OES, PCA-LDA, PLS and LS-SVM	Multi-elemental fingerprinting	(Esteki, Vander Heyden, et al., 2017)
	Addition of apricot kernel	GC-FID, PCA-LDA, PLS and LS-SVM	Fatty acid profile	(Esteki, Farajmand, et al., 2017)
Pistachio	Iranian varieties authentication	Trained sensory panel, PCA, LDA and PNN	Sensory attributes	(Ghasemi-Varnamkhasti, 2015)
	Addition of green pea granules	FT-Raman hyperspectral imaging, PCA and PLS	Spectral bands at 1655 and 1441 cm^{-1}	(Eksi-Kocak, Montes-Yilmaz, & Boyaci, 2016)
Hazelnut	Protected Designation of Origin (PDO) authentication	Near infrared spectra, PCA, KNN, SVM-DA, SIMCA and PLS-DA	Spectral data from 1100 to 2300 nm	(Moschetti, et al., 2015)
Peanut	Discrimination of peanut from commercial cereals, legumes, oilseeds and nuts	NIR, PC and PLS-DA	Spectral data from 896 to 1686 nm.	(Ghosh, et al., 2016)
	Addition of non-fresh peanuts	An array of 18 metal-oxide based gas sensors, PCA, LDA, SVM and PLS	e-nose data and volatile compounds (mainly aldehydes and ketones), acid value, peroxide value and content of crude fat	(Xu, et al., 2017)

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Highlights:

- Authentication of fat food products are a crucial issue for processing industries and consumers.
- Current protocols for the detection of fat food frauds are summarized.
- Chromatography-mass spectrometry methods are used to detect fat food frauds.
- Spectroscopic techniques are also proposed for the detection of fat food frauds.
- Multivariate analysis is used to identify the authenticity of fat food products.